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(54)

Sorbent složený z aktivní složky a pojivě organické matrice a způsob jeho výroby.

(57)

Sorbent složený z aktivní složky a pojivě organické matrice, přičemž pojivě matrice je tvořena polymerem nebo kopolymerem akrylonitrilu obsahujícím alespoň 40 %, výhodně 85 % akrylonitrilových jednotek. Způsob výroby sorbentu spočívá ve smísení aktivní látky s roztokem polymeru nebo kopolymeru akrylonitrilu. Vzniklá viskózní kapalina se vnáší do vodné erázací lázně.

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The patent relates to a sorbent consisting of an active component and a binding organic matrix, in which the active part is deposited in the form of small particles with a relatively large active surface and to a method of manufacturing same.

The main disadvantage in the use of active materials alone, without a binding matrix, lies in the fact that the sorbent surface is small in relation to its mass, and the mechanical stability and granulometric characteristics are not satisfactory for use in columns. It has therefore been proposed to use binding matrices where the active matter can be finely scattered which radically increases its surface area. Matrices must of course be permeable for sorbed matter and this usually also mean water. For this reason matrices of organic hydrogel have been developed and proved useful, for example V. Stoy and others, Czechoslovak Author's Copyright No. 181 605, where it was possible to directly coagulate the active substances into colloidal precipitates with an extremely large surface. The disadvantage of the matrices described in this copyright is their relatively small radiation stability so that the matrix may decay after a period of use, having previously changed its swelling capacity in water. Another disadvantage is that the soft, strongly swelling hydrogels deform in operation due to the pressure of column contents, which causes reduction of flow or blockage, especially in tall columns. Similar shortcomings are also shown in matrices consisting of other hydrogels, for example U.S. patent 3 284 238 dated 1966, author M. L. White. Other matrices from polyvinylalcohol, a Japanese patent No. 20 823 dated 1963, or polyvinylacetate and other non-cure resins, Czechoslovak Copyright No. 140 896, also have certain disadvantages. Polyvinylalcohol is partially soluble in water and is rapidly flushed out, especially at higher temperatures, whilst polyvinylacetate is not very permeable for aqueous solutions so that the active component is only effective near the grain surfaces. In this case therefore only a certain amount of binding agent must be used to connect only the individual particles of the active component, ref. J. Stejskal and others, Improved Inorganic Ion Exchangers, J. Radioanal. Chem., Vol. 31, 1974, pp. 371 to 379. Other organic binders described included the use of urea-formaldehyde resin, Czechoslovak Copyright No. 201 705, which produces, after hardening and product crushing, significantly separate, angular particles, with uneven life and

limited water perm ability, resulting in imperfect use of the active component. Polycondensation resins containing sulphonated phenol with formaldehyde enable the preparation of spherical particles of composite sorbent but this process is laborate and therefore disadvantageous; there is the need to perfectly wash the oil out of the product, whilst the process only allows preparation of a sorbent with a low active component content. The use of pearl cellulose as a binding polymer, Czechoslovak Copyright No. 228 489, has its serious disadvantage in the fact that the resulting product is not sufficiently strong and is limited to certain types of active sorbent component.

The above mentioned disadvantages are substantially reduced by a sorbent consisting of an active component and binding organic matrix, in which the active component is deposited in the form of small particles with relatively large active surface, and by the method for manufacturing same in accordance with the patent. Its principle is based on the fact that the binding matrix is formed from an acrylonitrile polymer or copolymer, containing at least 40%, but not more than 85% acrylonitrile units. The method of sorbent manufacture comprises mixing the active matter or its components with the acrylonitrile polymer or copolymer solution and introducing the resulting viscous liquid into an aqueous precipitation bath, optionally containing the second component of the active matter. The size of the sorbent macropores is controlled by setting the temperature of the precipitation bath below 70°C. The precipitation rate is controlled by adjusting the concentration of the polyacrylonitrile solvent in the precipitation bath.

The binding organic matrix, comprising polyacrylonitrile or acrylonitrile copolymer, is precipitated by water or by aqueous solutions under conditions which create a macroporous to spongy polymer. The pore size may be controlled either by the temperature of precipitation bath or by adding organic polyacrylonitrile solvents, or optionally inorganic salts or acids, especially those which are good solvents for polyacrylonitrile in concentrated aqueous solutions. It is understood that the concentration of these substances must not exceed the value at which no further precipitation takes place, but only the dilution of the polymer solution. Added ancillary substances are always water soluble and may, if necessary in individual cases, be removed by washing with water. Examples of organic solvents for polyacrylonitrile with unlimited miscibility with water include dimethylsulphoxide or dimethylformamide. The higher the content of the above mentioned addition in the precipitation bath, the smaller the size of th

pores, until at a certain value of concentration, which is characteristic for each of the substances added and easily identifiable by a simple experiment, the visible pores completely disappear. These values are generally given in sources dealing with the manufacture of acrylic fibres by a wet process, using a variety of solvents.

If temperature is used to control the pore size, the rule is that the precipitating bath temperature must be always above the value at which aquagel is formed, that is a precipitant containing only invisible interchain spaces filled by the precipitating bath and no visible macropores, which would manifest themselves by loss of translucency to transparency, by white staining and by a substantial reduction of tensile strength.

Matrices from polymers and acrylonitrile copolymers, which are practically non-hydrophilic, unless they were intentionally hydrophilized by a partial hydrolysis for example, enable access of aqueous solutions to the active component of the sorbent, which they surround, even though they may have dried prior to the usage. However, permeability for aqueous solutions and water may be significantly increased if drying never takes place so that following its manufacture, the sorbent is maintained in a moist condition throughout all manipulation, including transportation.

To achieve satisfactory permeability for aqueous liquids, the thin, originally at least partially continuous walls of the precipitated sorbent between individual macropores may be broken down by mechanical compression followed by relaxation, whilst both these actions must be carried out under moist conditions, or better still in excess aqueous solution or water.

A matrix of non-hydrolysed acrylonitrile polymers and copolymers is advantageous for its great chemical and radiation stability, ease of sorbent preparation with relatively high content of active matter and sufficient mechanical strength and abrasion resistance in columns during transportation. Several easily usable variable factors, primarily composition and temperature of precipitation bath, enable the adaptation of sorbent properties for various uses. Active matter may be mixed with acrylonitrile polymer or copolymer solution, prior to precipitation, or active matter may be created in the precipitate in colloidal state by analogous methods, which are described in the Czechoslovak Copyright No. 181 605, i.e. for example by precipitation, where one component of the active matter is mixed with the acrylonitrile polymer or copolymer solution and the second component, with which it forms the precipitate, is

dissolved in the precipitation bath. If the polymer precipitate was not dried prior to this, the active matter may be precipitated in the precipitate as well as in a separate bath. After drying or heating the moist precipitate to above 70°C the precipitation of active matter is no longer satisfactory when immersed in the solution of the second component. Such heating also slows down and reduces the quality of entry of the treated liquid to the active sorbent component.

Acrylonitrile polymers and copolymers may be used in any form, for example as a powder obtained by emulsion polymerisation or copolymerisation of acrylonitrile in water, as solutions obtained by direct polymerisation or by copolymerisation of acrylonitrile in a solvent, for example in a 50% to 60% aqueous solution of sodium rhodanide in water, in a 70% aqueous solution of zinc chloride or in at least 50% aqueous nitric acid. In this last case it is necessary to carry out polymerisation as quickly as possible and use the resultant solution immediately to prevent significant partial hydrolysis of the polyacrylonitrile. Suitable forms are various wastes, for example of films or textile fibres. These polymers are dissolved in an appropriate solvent, for example in dimethylsulphoxide or in any of the above mentioned inorganic solvents, mixed with the active matter of the sorbent or with its component, from which the colloidal sorbent is formed by the action of the second component dissolved in the precipitation bath or in a separate solution.

The advantages are primarily the universality of the above described processes, their accessibility and low cost of materials used, whilst the treated sorbents possess good granulometric properties which may easily be altered according to requirements. The used matrix does not negatively affect the sorption rate nor the capacity of used active component. As a consequence of considerable porosity the granulated sorbents may contain up to 50 % by weight of water whilst maintaining sufficient strength, which enables complete use of the active component, whose content in the solids of treated sorbent may reach up to 95% by weight. Given modifications of the described method can provide treatment of all known sorbents such as both natural and synthetic aluminosilicates, hydrated oxides of polyvalent elements, polyvalent element salts and polybasic inorganic acid salts with low solubility, heteropolyacid salts, sodium titanate and other compounds with low solubility in aqueous solutions, and materials used as sorbents. Use of the patent is not restricted to certain active components but only to their combination with macroporous polyacrylonitrile and its copolymers as a binder, and to the method of sorbent treatment.

enabling the formation of active component directly in the polymer, with the benefit of the active component being homogeneously dispersed as a colloidal particle in the sorbent granules. The method of sorbent manufacture according to this patent enables the use of powder sorbents in columns, improves the utilization of the active components of sorbents, increases the life of sorbent in production conditions and reduces the failure rate of sorption columns caused by crumbling of sorbents with the subsequent blockage or reduced flow through the column.

The sorbent and the method of its manufacture are explained in detail in the following examples.

#### **Example No. 1**

5 g of waste acrylonitrile staple containing minimum 85% polyacrylonitrile is dissolved in 100 g of 65% nitric acid at room temperature in 1 hour. The resulting solution is mixed with 30 g of powder ammonium molybdophosphate and the resulting mixture is expressed by a thin nozzle, whilst dispersion takes place by compressed air into the excess aqueous solution of ammonium nitrate (1 g  $\text{NH}_4\text{NO}_3$  in  $\text{dm}^3$ ), which is maintained in a swirling motion. After washing with water sorbent is stored in a swelled condition and may be used for selective concentration of radioactive cesium from aqueous solutions in columns under high stress.

#### **Example No. 2**

Powder polyacrylonitrile with average molecular weight of 300,000 is dissolved in anhydrous dimethylsulphoxide to provide a 7.5% solution. 100 g of this solution is mixed with 50 g of dehydrated titanium dioxide or sodium titanate with grain size smaller than 0.1 mm. The resulting mixture is expressed into lightly agitated aqueous bath whilst simultaneously carrying out dispersion with compressed air. The resulting sorbent granules are left in the aqueous bath for several hours and constantly lightly agitated. The swelled sorbent is suitable, after decanting, for separation of  $^{90}\text{Sr}$ ,  $^{226}\text{Ra}$  and other radionuclides from various types of waste water.

#### **Example No. 3**

The same method applies as described in Example No. 2, except that polyacrylonitrile staple is used to prepare the solution of binding polymer, and dehydrated and crushed synthetic or natural aluminosilicate as an active component. The resulting mixture

is expressed into a bath containing 5 to 10% aqueous solution of dimethylsulphoxide.

#### Example No. 4

A powder polyacrylonitrile or waste polyacrylonitrile staple is dissolved in dimethylformamide to form a 10% solution. To 100 g of this solution is added 30 g of dehydrated and crushed hydrated antimonite oxide. The resulting mixture is continuously stirred and allowed to drip through a thin nozzle into an aqueous bath. The resulting globules are stirred for several hours. After decanting, the swollen sorbent is suitable for the selective separation of radiosodium.

#### Example No. 5

8.5 g of crushed potassium hexacyanoferrate and 7.5 g of crushed nickel chloride with grain size smaller than 0.1 mm is dried at 100°C for the period of 4 hours. After cooling it is mixed with 25 g of a 5% solution of acrylonitrile staple in dimethylsulphoxide. The resulting mixture is expressed by a nozzle, with simultaneous dispersion by compressed air into an aqueous bath, where sorbent granules are formed, containing as an active component the colloiddally dispersed potassium nickel hexacyanoferrate. After washing the polymer solvent and decanting the precipitate formed as a by-product, the sorbent is suitable for selective separation of radioactive cesium from radioactive waste with high concentration of ballast salts and varying acidity, in the range from diluted mineral acids up to pH 11.

#### Example No. 6

5 g of powder polyacrylonitrile with an average molecular weight of 100,000 is dissolved in 50 g of 65% nitric acid and the resulting solution is mixed with 20 g of crushed (triturate) powdered barium nitrate. The resulting mixture is dispersed by air into a bath of 10% sulphuric acid or sodium sulphate solution, maintained at a temperature of 50°C. Granulated sorbent containing colloiddally dispersed barium sulphate as an active component is decanted by water to remove the precipitant separated with the granulated product.

